

Structural study of six cycloalkylammonium cinnamate salt structures featuring one-dimensional columns and two-dimensional hydrogen-bonded networks

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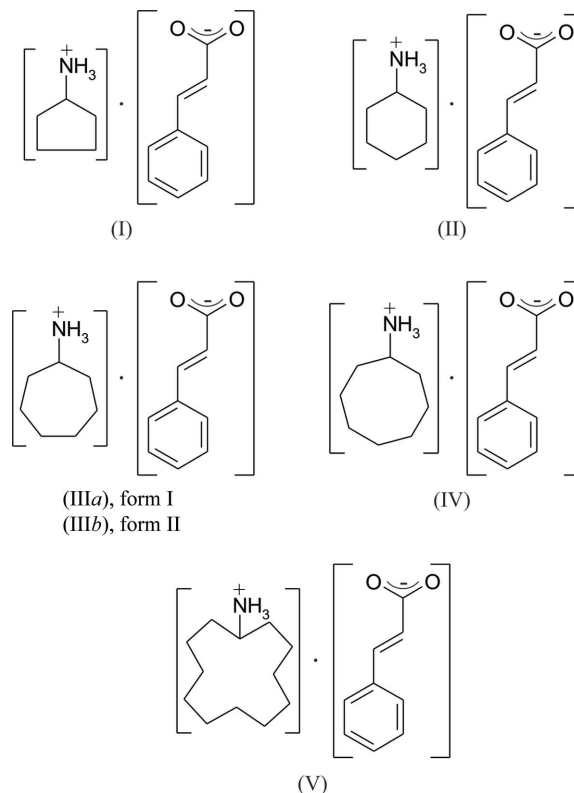
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Six ammonium carboxylate salts, namely cyclopentylammonium cinnamate, $C_5H_{12}N^+ \cdot C_9H_7O_2^-$, (I), cyclohexylammonium cinnamate, $C_6H_{14}N^+ \cdot C_9H_7O_2^-$, (II), cycloheptylammonium cinnamate form I, $C_7H_{16}N^+ \cdot C_9H_7O_2^-$, (IIIa), and form II, (IIIb), cyclooctylammonium cinnamate, $C_8H_{18}N^+ \cdot C_9H_7O_2^-$, (IV), and cyclododecylammonium cinnamate, $C_{12}H_{26}N^+ \cdot C_9H_7O_2^-$, (V), are reported. Salts (II)–(V) all have a 1:1 ratio of cation to anion and feature three $N^+ \cdots O^-$ hydrogen bonds forming one-dimensional hydrogen-bonded columns consisting of repeating $R_4^3(10)$ rings, while salt (I) has a two-dimensional network made up of alternating $R_4^4(12)$ and $R_8^6(20)$ rings. Salt (III) consists of two polymorphic forms, *viz.* form I having $Z' = 1$ and form II with $Z' = 2$. The latter polymorph has disorder of the cycloheptane rings in the two cations, as well as whole-molecule disorder of one of the cinnamate anions. A similar, but ordered, $Z' = 2$ structure is seen in salt (IV).

Comment

Understanding how to control the solid-state formation of molecules using a variety of intermolecular interactions is at the heart of crystal engineering (Tiekink *et al.*, 2010). Supramolecular synthesis makes use especially of the hydrogen bond, the most directional of the known intermolecular interactions (Aakeröy & Beatty, 2001). Concepts of crystal engineering have been applied in the synthesis of ammonium carboxylate salts of general formula $(R-NH_3^+) \cdot (R'-COO^-)$ to form hydrogen-bonded one-dimensional columns in the solid state (Lemmerer, 2008, 2011a,b,c; Nagahama *et al.*, 2003; Odendal *et al.*, 2010; Yuge *et al.*, 2008). The hydrogen bond observed in these molecular salts is the robust charge-assisted $N^+ \cdots H \cdots O^-$ interaction (Braga *et al.*, 2000), and three such hydrogen bonds can be formed from the primary ammonium cation to the carboxylate anion.

In the past, we have made one-dimensional columns using this type of hydrogen bond (Lemmerer *et al.*, 2010) and the most commonly encountered motif consists of repeating $R_4^3(10)$ rings (Fig. 1), described using graph-set notation (Bernstein *et al.*, 1995). The packing of columns is based on the close packing principle of bumps in hollows. Each individual column, when viewed down its length, resembles a cross, *X*, as the hydrogen-bonding functional groups point inward (centred at the centre of the cross) and the hydrocarbon parts



point outward, and the latter then interdigitate as best as possible with neighbouring columns (*X*). The counter-cations are cycloalkylammonium cations with ring sizes ranging from three- to 12-membered. So far, the anion has been planar and the carboxylate functional groups coplanar with the hydrocarbon backbone. In this study, we want to observe if similar hydrogen-bonded rings and assemblies are found for molecules where the carboxylate functional groups are extended further out from the ring, yet are still predominantly planar, by using cinnamic acid (3-phenylprop-2-enoic acid). To this end, we synthesized and characterized, using single-crystal X-ray

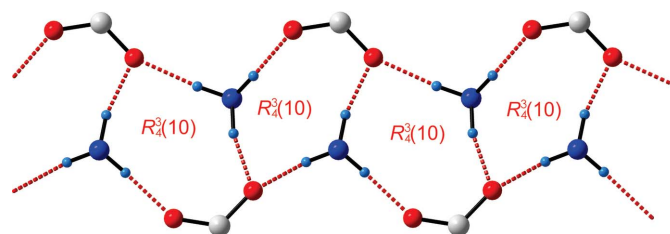


Figure 1
The most common type of ladder formed by ammonium carboxylate salts.

diffraction, six salts, namely cyclopentylammonium cinnamate, (I), cyclohexylammonium cinnamate, (II), cycloheptylammonium cinnamate form I, (III*a*), and form II, (III*b*), cyclooctylammonium cinnamate, (IV), and cyclododecylammonium cinnamate, (V). These six ammonium carboxylate salts were all prepared in an identical manner. A 1:1 stoichiometric ratio of amine to acid was dissolved in methanol and the crystals were grown by slow evaporation at room temperature. Since the hydrogen-bond interactions are central to this study, the H atoms on the ammonium group are all labelled consistently in order to make comparisons of the six structures easier. H1A on the ammonium group is always *trans* to the methine H10 atom on the cyclic hydrocarbon ring and forms a symmetry-independent hydrogen bond to O1 or O2 on the benzoate anion. Similarly, H2A is *trans* to the methine H atom, and forms a symmetry-independent hydrogen bond to O3 or O4 for those salts with $Z' = 2$. H1B and H1C are then labelled clockwise relative to H1A, viewed from N1 to the C atom of the hydrocarbon ring, and similarly for H2B and H2C. For the cinnamate anion, O1 is *anti* to the double bond and O2 is *syn*, and similarly for O3 and O4.

The molecular structure and atom-numbering scheme of the asymmetric unit of the 1:1 salt cyclopentylammonium cinnamate, (I), are shown in Fig. 2. The asymmetric unit consists of one cyclopentylammonium cation and one cinnamate anion, both on general positions. The cyclopentyl ring has an envelope conformation. The ammonium group forms three charge-assisted hydrogen bonds to form two types of rings: (i) an $R_4^4(12)$ ring, consisting of two ammonium cations and two carboxylate anions, involving atoms O1 and O2, and (ii) a second larger $R_8^6(20)$ ring using four cations, two anions using both O atoms and two anions using only one O atom (Fig. 3*a*). This hydrogen-bond pattern leads to a two-dimensional network parallel to the *ab* plane, which has the hydrocarbon ends of the ions approximately perpendicular to the hydrogen-bonded layers. Adjacent layers are interdigitated through the aromatic rings of the cinnamate anions (Fig. 3*b*).

The molecular structure and atom-numbering scheme of the asymmetric unit of the 1:1 salt cyclohexylammonium cinnamate, (II), are shown in Fig. 4. The asymmetric unit consists of one cyclohexylammonium cation and one cinnamate anion, both on general positions. The cyclohexyl ring has a chair conformation. The ammonium group forms three charge-assisted hydrogen bonds to form a ring [graph-set notation $R_4^3(10)$] consisting of two ammonium cations and two carboxylate anions, one involving both atoms O1 and O2 and the second involving only atom O2 (see Fig. 5*a*). All three ammonium H atoms are used to form the rings and atom O2 acts as a bifurcated hydrogen-bond acceptor and forms a symmetry-independent hydrogen bond to H1A. This hydrogen-bond pattern has translational symmetry *via* a twofold screw axis along the crystallographic *b* axis inherent in the space group $P2_1/n$, leading to one-dimensional hydrogen-bonded columns. The columns pack closely by interdigitation of the cyclohexane and aromatic rings (Fig. 5*b*).

The molecular structure and atom-numbering scheme of the asymmetric unit of form I of the 1:1 salt cycloheptylammonium cinnamate, (III*a*), are shown in Fig. 6. The asymmetric unit consists of one cycloheptylammonium cation and one cinnamate anion, both on general positions. The cycloheptyl ring has a chair conformation. The ammonium group forms three charge-assisted hydrogen bonds to form a ring [graph-set notation $R_4^3(10)$] consisting of two ammonium cations and two carboxylate anions, one involving both atoms O1 and O2 and the second involving only atom O2 (see Fig. 5*a*). All three ammonium H atoms are used to form the rings and atom O2 acts as a bifurcated hydrogen-bond acceptor and forms a symmetry-independent hydrogen bond to H1A. This hydrogen-bond pattern has translational symmetry *via* a twofold screw axis along the crystallographic *b* axis inherent in the space group $P2_1/n$, leading to one-dimensional hydrogen-bonded columns. The columns pack closely by interdigitation of the cyclohexane and aromatic rings (Fig. 5*b*).

The molecular structure and atom-numbering scheme of the asymmetric unit of form I of the 1:1 salt cycloheptylammonium cinnamate, (III*a*), are shown in Fig. 6. The asymmetric unit consists of one cycloheptylammonium cation and one cinnamate anion, both on general positions. The cycloheptyl ring has a chair conformation. The ammonium group forms three charge-assisted hydrogen bonds to form a ring [graph-set notation $R_4^3(10)$] consisting of two ammonium cations and two carboxylate anions, one involving both atoms O1 and O2 and the second involving only atom O2 (see Fig. 5*a*). All three ammonium H atoms are used to form the rings and atom O2 acts as a bifurcated hydrogen-bond acceptor and forms a symmetry-independent hydrogen bond to H1A. This hydrogen-bond pattern has translational symmetry *via* a twofold screw axis along the crystallographic *b* axis inherent in the space group $P2_1/n$, leading to one-dimensional hydrogen-bonded columns. The columns pack closely by interdigitation of the cyclohexane and aromatic rings (Fig. 5*b*).

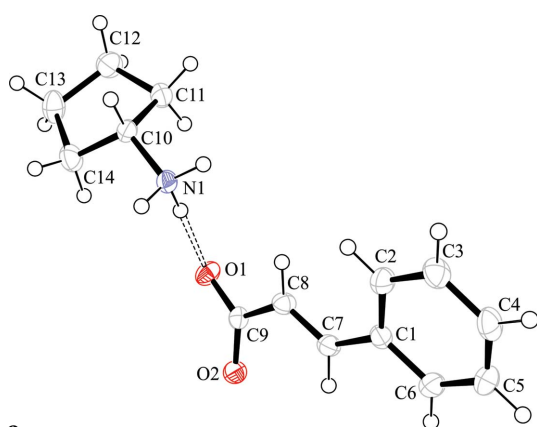
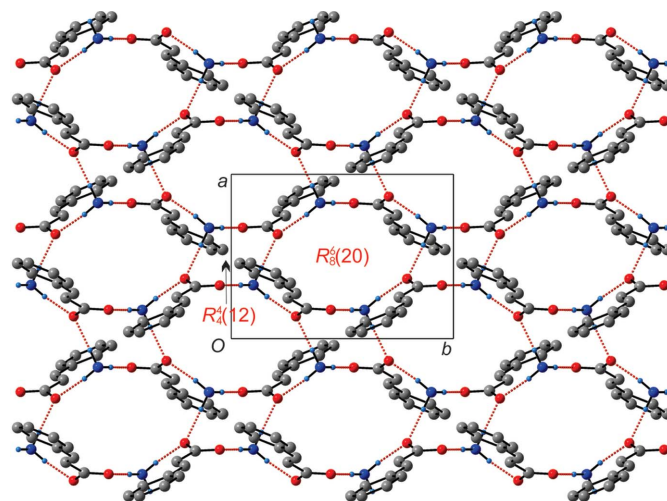
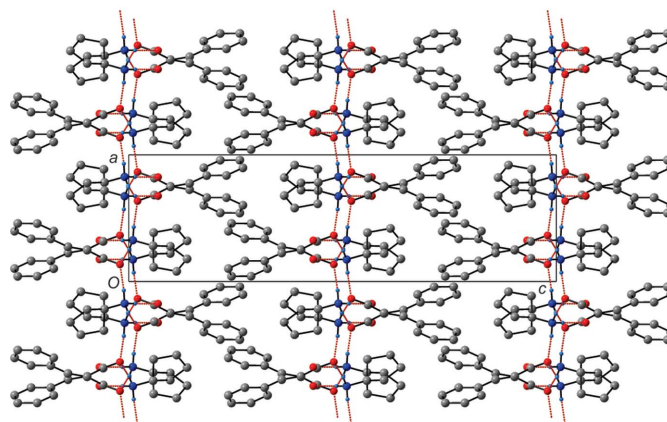


Figure 2

A perspective view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius. The dashed line indicates the symmetry-independent $N^+ - H \cdots O^-$ hydrogen bond.



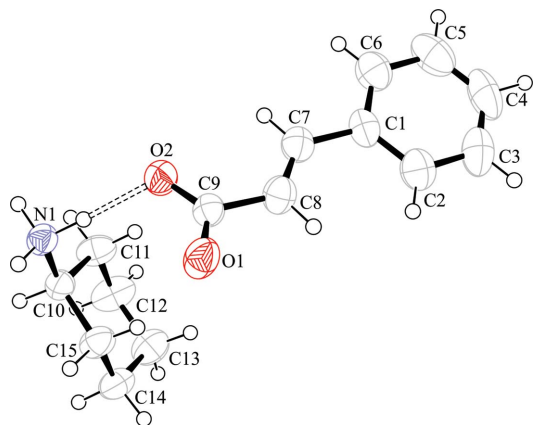
(a)



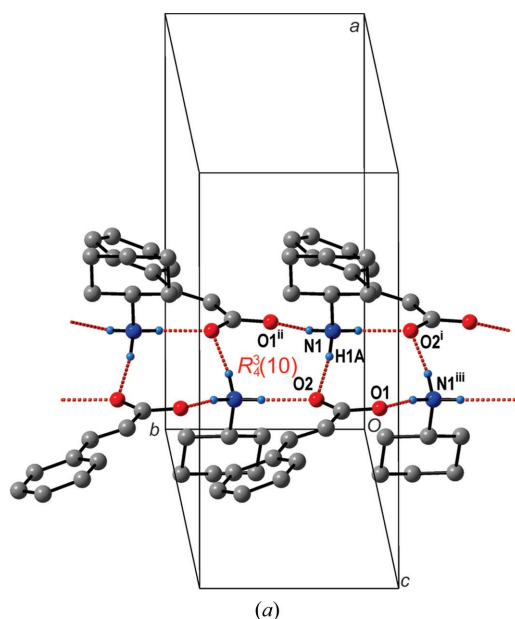
(b)

Figure 3

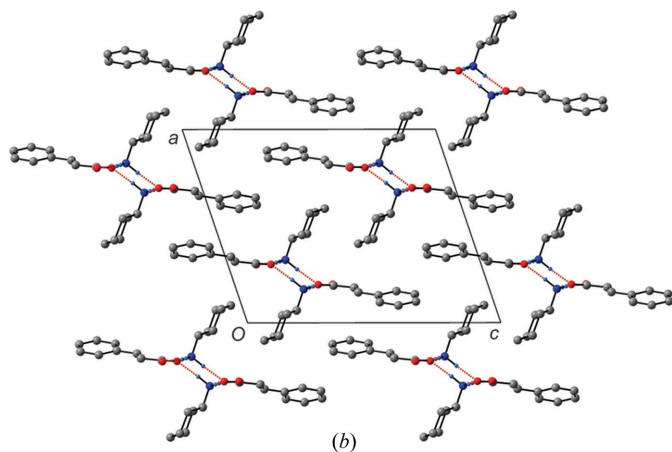
(a) View of the two-dimensional hydrogen-bonded layer formed by the $R_4^4(12)$ and $R_8^6(20)$ rings in (I). The hydrocarbon ring of the cation has been omitted for clarity. (b) The packing of the layers, interdigitated through the cinnamate anions. H atoms not involved in hydrogen bonding have been omitted for clarity.


Figure 4

A perspective view of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius. The dashed line indicates the symmetry-independent $N^+ - H \cdots O^-$ hydrogen bond.



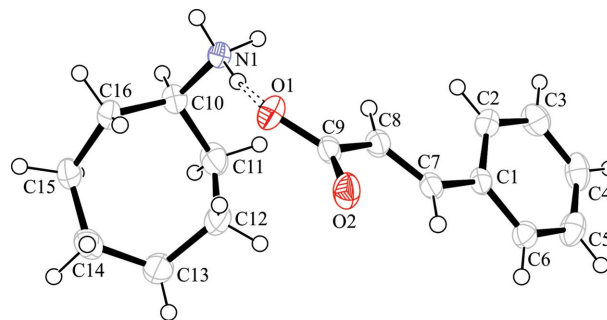
(a)



(b)

Figure 5

(a) The $R_4^3(10)$ rings forming a one-dimensional column in (II). (b) Packing diagram of the columns, with H atoms not involved in hydrogen bonding omitted for clarity.


Figure 6

A perspective view of (IIIa), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius. The dashed line indicates the symmetry-independent $N^+ - H \cdots O^-$ hydrogen bond.

metric unit consists of one cycloheptylammonium cation and one cinnamate anion, both on general positions. The cycloheptyl ring has a twist-boat conformation. The ammonium group forms three charge-assisted hydrogen bonds to form a ring [graph-set notation $R_4^3(10)$] consisting of two ammonium cations and two carboxylate anions, one involving both atoms O1 and O2 and the second involving only atom O1, different to (II). All three ammonium H atoms are used to form the rings and atom O1 acts as a bifurcated hydrogen-bond acceptor and forms a symmetry-independent hydrogen bond to H1A in this case. This hydrogen-bond pattern has translational symmetry *via* a twofold screw axis along the crystallographic a axis inherent in the space group $P2_12_12_1$, and forms one-dimensional hydrogen-bonded columns. The columns pack closely by interdigitation of the cycloheptyl and aromatic rings (Fig. 7).

The molecular structure and atom-numbering scheme of the asymmetric unit of form II of the 1:1 salt cycloheptylammonium cinnamate, (IIIb), are shown in Fig. 8. The asymmetric unit consists of two cycloheptylammonium cations (labelled N1 and N2) and two cinnamate anions (labelled O1/O2 and O3/O4), all on general positions. Both N1 and N2 cations have two ring C atoms split over two positions, such that the cycloheptyl rings adopt one of two twist-chair conformations. The cinnamate anion O1/O2 features whole-molecule disorder. The second anion is completely ordered. In the descriptions of the hydrogen bonding, we will focus on the major parts of the disordered components. Both sets of cation/anion pairs form $R_4^3(10)$ rings, as seen in (II), where the symmetry-independent hydrogen bonds from H1A and H2A are to O2 and O4, respectively. This leads to two symmetry-independent one-dimensional columns, running along the b axis, and which again interdigitate through the cycloheptyl and aromatic rings (Fig. 9).

The molecular structure and atom-numbering scheme of the asymmetric unit of the 1:1 salt cyclooctylammonium cinnamate, (IV), are shown in Fig. 10. The asymmetric unit consists of two cyclooctylammonium cations (labelled N1 and N2) and two cinnamate anions (labelled O1/O2 and O3/O4), all on general positions. Both N1 and N2 cations have boat-chair conformations. Both sets of cation/anion pairs form $R_4^3(10)$ rings, as seen in (IIIb), where the symmetry-independent

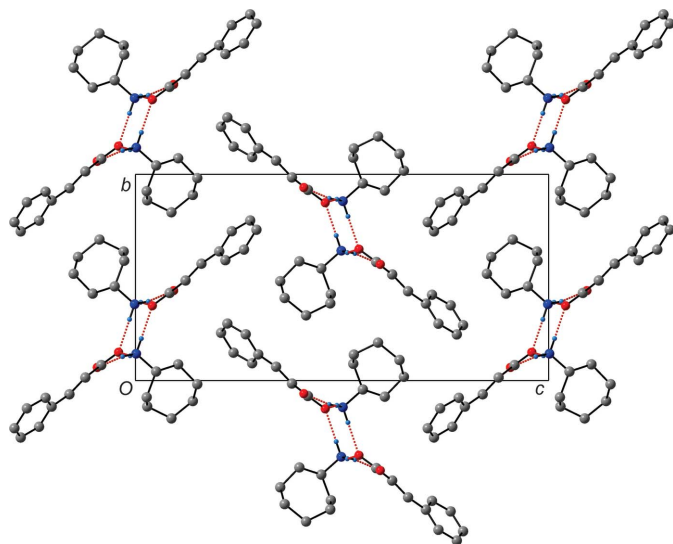


Figure 7
Packing of the hydrogen-bonded columns in (IIIa), formed by repeating $R_4^3(10)$ rings. H atoms not involved in hydrogen bonding have been omitted for clarity.

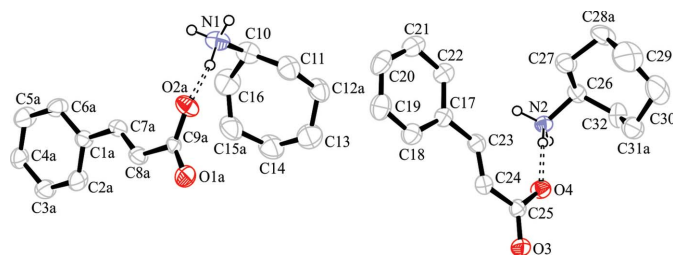


Figure 8
A perspective view of (IIIb), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius. The dashed line indicates the symmetry-independent $N^+ - H \cdots O^-$ hydrogen bond. Only the major parts of the disorder are shown, and C-bound H atoms have been omitted for clarity.

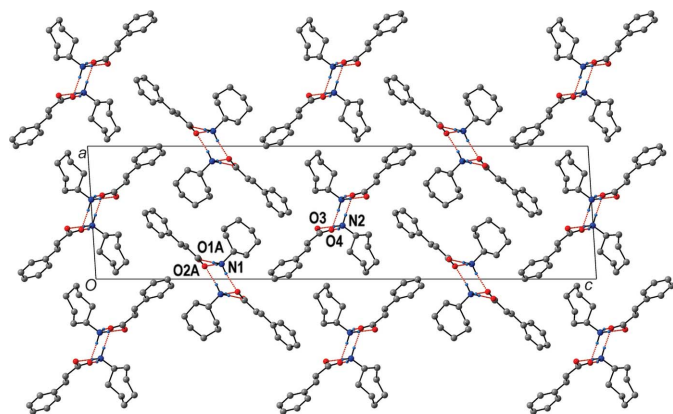


Figure 9
Packing of the two symmetry-independent hydrogen-bonded columns in (IIIb), formed by repeating $R_4^3(10)$ rings. Note the alternating pattern along the c axis of the two columns. H atoms not involved in hydrogen bonding have been omitted for clarity.

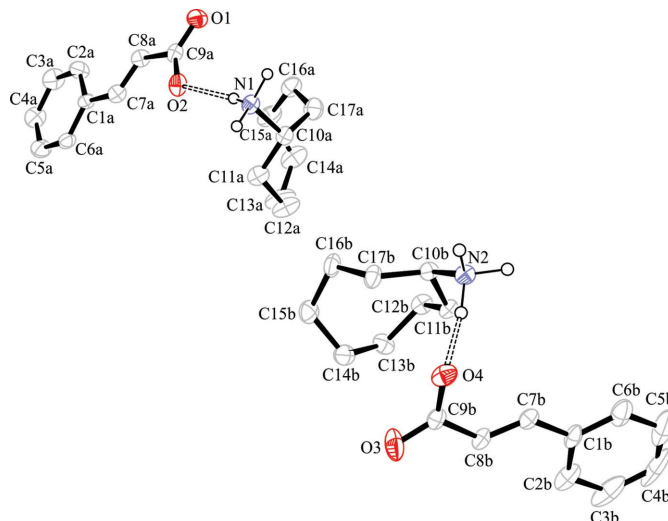


Figure 10
A perspective view of (IV), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius. The dashed line indicates the symmetry-independent $N^+ - H \cdots O^-$ hydrogen bond. C-bound H atoms have been omitted for clarity.

hydrogen bonds from H1A and H2A are to O2 and O4, respectively. This leads to two symmetry-independent one-dimensional columns, running along the b axis, which again interdigitate through the cyclooctyl and aromatic rings (Fig. 11).

The molecular structure and atom-numbering scheme of the asymmetric unit of the 1:1 salt cyclododecylammonium cinnamate, (V), are shown in Fig. 12. The asymmetric unit consists of one cyclododecylammonium cation and one cinnamate anion, both on general positions. The ammonium group forms three charge-assisted hydrogen bonds to form a ring [graph-set notation $R_4^3(10)$] consisting of two ammonium cations and two carboxylate anions, one involving both atoms O1 and O2 and the second involving only atom O1, as seen in (IIIa). All three ammonium H atoms are used to form the rings, and atom O1 acts as a bifurcated hydrogen-bond

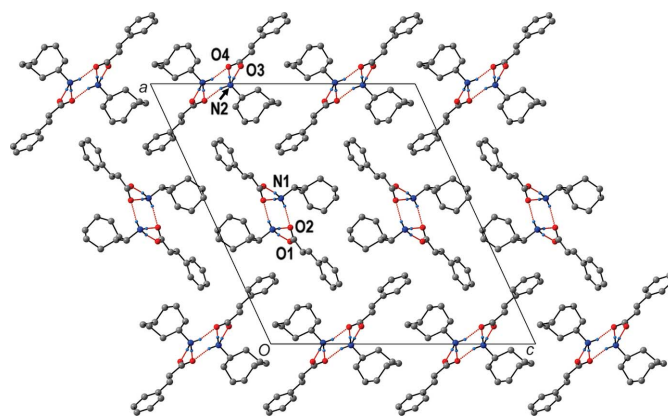


Figure 11
Packing of the hydrogen-bonded columns in (IV), formed by repeating $R_4^3(10)$ rings. H atoms not involved in hydrogen bonding have been omitted for clarity.

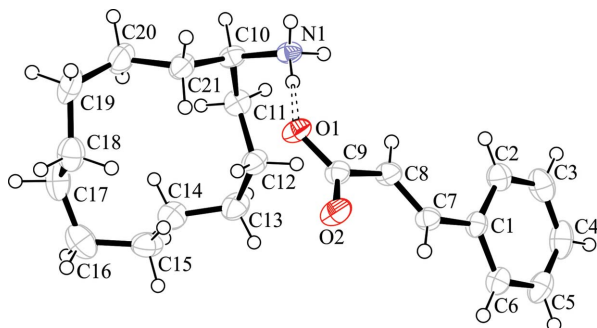


Figure 12
A perspective view of (V), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius. The dashed line indicates the symmetry-independent $N^+ \cdots O^-$ hydrogen bond.

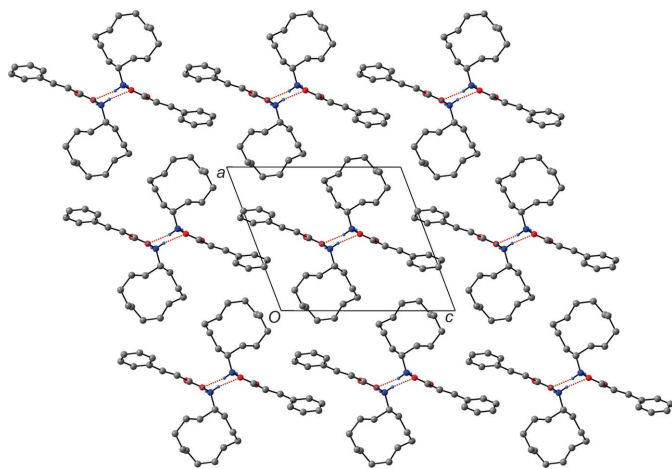


Figure 13
Packing of the hydrogen-bonded columns in (V), formed by repeating $R_3^3(10)$ rings. H atoms not involved in hydrogen bonding have been omitted for clarity.

acceptor and forms a symmetry-independent hydrogen bond to H1A in this case. This hydrogen-bond pattern has translational symmetry *via* a twofold screw axis along the crystallographic *b* axis inherent in the space group $P2_1$, and forms one-dimensional hydrogen-bonded columns. The columns pack closely by interdigitation of the cyclododecyl and aromatic rings (Fig. 13).

Experimental

All chemicals were purchased from commercial sources and were used as received. Crystals were grown under ambient conditions by slow evaporation of a methanol solution containing a 1:1 ratio of amine and acid. Detailed masses and volumes are as follows: for (I), cyclopentylamine (0.115 g, 1.35 mmol) and cinnamic acid (0.200 g, 1.35 mmol) in methanol (8 ml); for (II), cyclohexylamine (0.134 g, 1.35 mmol) and cinnamic acid (0.200 g, 1.35 mmol) in methanol (8 ml); for (III*a*), cycloheptylamine (0.153 g, 1.35 mmol) and cinnamic acid (0.200 g, 1.35 mmol) in methanol (8 ml); for (III*b*), cycloheptylamine (0.153 g, 1.35 mmol) and cinnamic acid (0.200 g, 1.35 mmol) dissolved in hot methanol (8 ml) using sonication for 2 min; for (IV), cyclooctylamine (0.172 g, 1.35 mmol) and cinnamic

acid (0.200 g, 1.35 mmol) in methanol (8 ml); for (V), cyclododecylamine (0.248 g, 1.35 mmol) and cinnamic acid (0.200 g, 1.35 mmol) in methanol (8 ml).

Compound (I)

Crystal data

$C_5H_{12}N^+ \cdot C_9H_7O_2^-$
 $M_r = 233.3$
Orthorhombic, $Pbca$
 $a = 8.2523 (3) \text{ \AA}$
 $b = 11.1475 (3) \text{ \AA}$
 $c = 27.8170 (7) \text{ \AA}$

$V = 2558.96 (13) \text{ \AA}^3$
 $Z = 8$
Mo $K\alpha$ radiation
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 173 \text{ K}$
 $0.55 \times 0.4 \times 0.1 \text{ mm}$

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.957$, $T_{\max} = 0.992$

14051 measured reflections
3092 independent reflections
2170 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.107$
 $S = 1.02$
3092 reflections
163 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.21 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.20 \text{ e \AA}^{-3}$

Compound (II)

Crystal data

$C_6H_{14}N^+ \cdot C_9H_7O_2^-$
 $M_r = 247.33$
Monoclinic, $P2_1/n$
 $a = 13.4992 (4) \text{ \AA}$
 $b = 6.4723 (2) \text{ \AA}$
 $c = 16.7352 (5) \text{ \AA}$
 $\beta = 108.610 (2)^\circ$

$V = 1385.72 (7) \text{ \AA}^3$
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 173 \text{ K}$
 $0.5 \times 0.26 \times 0.06 \text{ mm}$

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.962$, $T_{\max} = 0.995$

14450 measured reflections
3348 independent reflections
1957 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.134$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1A \cdots O1$	0.921 (16)	1.866 (16)	2.7824 (15)	172.4 (14)
$N1-H1B \cdots O1^i$	0.949 (17)	1.900 (17)	2.8471 (15)	175.6 (12)
$N1-H1C \cdots O2^{ii}$	0.928 (15)	1.830 (15)	2.7519 (13)	171.6 (13)

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, z$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1A \cdots O2$	1.00 (2)	1.80 (2)	2.7878 (19)	172.0 (15)
$N1-H1B \cdots O2^i$	0.93 (2)	1.86 (2)	2.7907 (19)	175.1 (17)
$N1-H1C \cdots O1^{ii}$	0.96 (2)	1.76 (2)	2.7123 (18)	170.1 (18)

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.174$
 $S = 0.99$
 3348 reflections
 172 parameters

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$

Compound (IIIa)
Crystal data

$\text{C}_7\text{H}_{16}\text{N}^+\cdot\text{C}_9\text{H}_7\text{O}_2^-$
 $M_r = 261.35$
 Orthorhombic, $P2_12_12_1$
 $a = 5.7790 \text{ (4) } \text{\AA}$
 $b = 11.3400 \text{ (11) } \text{\AA}$
 $c = 22.7510 \text{ (15) } \text{\AA}$

$V = 1491.0 \text{ (2) } \text{\AA}^3$
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 173 \text{ K}$
 $0.59 \times 0.14 \times 0.05 \text{ mm}$

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: integration (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.957$, $T_{\max} = 0.996$

5537 measured reflections
 2094 independent reflections
 1513 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.084$
 $S = 0.95$
 2094 reflections
 181 parameters

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max} = 0.14 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$

Compound (IIIb)
Crystal data

$\text{C}_7\text{H}_{16}\text{N}^+\cdot\text{C}_9\text{H}_7\text{O}_2^-$
 $M_r = 261.35$
 Monoclinic, $P2_1/c$
 $a = 11.4496 \text{ (2) } \text{\AA}$
 $b = 6.1011 \text{ (1) } \text{\AA}$
 $c = 43.0883 \text{ (8) } \text{\AA}$
 $\beta = 93.659 \text{ (1)}^\circ$

$V = 3003.80 \text{ (9) } \text{\AA}^3$
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 173 \text{ K}$
 $0.45 \times 0.3 \times 0.21 \text{ mm}$

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.967$, $T_{\max} = 0.984$

37019 measured reflections
 7152 independent reflections
 4684 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.149$
 $S = 1.06$
 7152 reflections
 487 parameters
 31 restraints

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$

Table 3

 Hydrogen-bond geometry (\AA , $^\circ$) for (IIIa).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1A}\cdots\text{O1}$	0.99 (2)	1.76 (2)	2.739 (2)	167 (2)
$\text{N1}-\text{H1B}\cdots\text{O1}^{\text{i}}$	0.89 (3)	1.92 (3)	2.805 (2)	178 (2)
$\text{N1}-\text{H1C}\cdots\text{O2}^{\text{ii}}$	1.01 (2)	1.75 (2)	2.741 (2)	166 (2)

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (ii) $x + 1, y, z$.

Table 4

 Hydrogen-bond geometry (\AA , $^\circ$) for (IIIb).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1A}\cdots\text{O2A}$	0.98 (2)	1.80 (2)	2.768 (7)	170.7 (17)
$\text{N1}-\text{H1B}\cdots\text{O1A}^{\text{i}}$	0.96 (2)	1.62 (2)	2.578 (6)	175.6 (19)
$\text{N1}-\text{H1C}\cdots\text{O2A}^{\text{ii}}$	0.91 (2)	1.95 (2)	2.854 (6)	168.0 (18)
$\text{N1}-\text{H1A}\cdots\text{O1B}$	0.98 (2)	1.81 (2)	2.775 (9)	172.0 (17)
$\text{N1}-\text{H1B}\cdots\text{O2B}^{\text{i}}$	0.96 (2)	1.99 (2)	2.945 (9)	170.0 (18)
$\text{N1}-\text{H1C}\cdots\text{O1B}^{\text{ii}}$	0.91 (2)	1.73 (2)	2.639 (9)	174.4 (19)
$\text{N2}-\text{H2A}\cdots\text{O4}$	0.953 (18)	1.846 (18)	2.7783 (16)	165.3 (14)
$\text{N2}-\text{H2B}\cdots\text{O4}^{\text{iii}}$	0.962 (18)	1.867 (18)	2.8205 (16)	170.8 (15)
$\text{N2}-\text{H2C}\cdots\text{O3}^{\text{i}}$	0.986 (17)	1.745 (17)	2.7277 (16)	174.7 (15)

Symmetry codes: (i) $x, y + 1, z$; (ii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, -y, -z + 1$.

Compound (IV)
Crystal data

$\text{C}_8\text{H}_{18}\text{N}^+\cdot\text{C}_9\text{H}_7\text{O}_2^-$
 $M_r = 275.38$
 Monoclinic, $P2_1/c$
 $a = 24.4790 \text{ (4) } \text{\AA}$
 $b = 6.2800 \text{ (4) } \text{\AA}$
 $c = 22.6340 \text{ (5) } \text{\AA}$
 $\beta = 114.894 \text{ (2)}^\circ$

$V = 3156.2 \text{ (2) } \text{\AA}^3$
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 173 \text{ K}$
 $0.55 \times 0.03 \times 0.02 \text{ mm}$

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: integration (*XPREF*; Bruker, 2004)
 $T_{\min} = 0.975$, $T_{\max} = 0.999$

15558 measured reflections
 4649 independent reflections
 2044 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.208$
 $\theta_{\max} = 23.5^\circ$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.060$
 $wR(F^2) = 0.160$
 $S = 0.86$
 4649 reflections
 379 parameters

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$

Compound (V)
Crystal data

$\text{C}_{12}\text{H}_{26}\text{N}^+\cdot\text{C}_9\text{H}_7\text{O}_2^-$
 $M_r = 331.48$
 Monoclinic, $P2_1$
 $a = 12.6990 \text{ (4) } \text{\AA}$
 $b = 5.8910 \text{ (2) } \text{\AA}$
 $c = 14.387 \text{ (4) } \text{\AA}$
 $\beta = 110.855 \text{ (2)}^\circ$

$V = 1005.8 \text{ (3) } \text{\AA}^3$
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.07 \text{ mm}^{-1}$
 $T = 173 \text{ K}$
 $0.59 \times 0.11 \times 0.07 \text{ mm}$

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: integration (*XPREF*; Bruker, 2004)
 $T_{\min} = 0.969$, $T_{\max} = 0.996$

7908 measured reflections
 2665 independent reflections
 2137 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.096$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.124$
 $S = 1.00$
 2665 reflections
 226 parameters
 1 restraint

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max} = 0.19 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$

Table 5
Hydrogen-bond geometry (Å, °) for (IV).

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
N1—H1A···O2	0.78 (5)	1.99 (5)	2.755 (5)	166 (5)
N1—H1B···O2 ⁱ	1.03 (4)	1.72 (4)	2.751 (5)	177 (4)
N1—H1C···O1 ⁱⁱ	1.08 (4)	1.70 (4)	2.771 (5)	171 (3)
N2—H2A···O4	1.05 (4)	1.72 (4)	2.766 (5)	171 (3)
N2—H2B···O4 ⁱⁱⁱ	0.88 (4)	1.89 (4)	2.737 (4)	163 (4)
N2—H2C···O3 ^{iv}	1.11 (4)	1.64 (4)	2.739 (5)	170 (3)

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x, y - 1, z$.

Table 6
Hydrogen-bond geometry (Å, °) for (V).

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
N1—H1A···O1	0.93 (3)	1.81 (3)	2.736 (3)	170 (3)
N1—H1B···O1 ⁱ	0.81 (3)	2.00 (3)	2.786 (3)	165 (3)
N1—H1C···O2 ⁱⁱ	0.96 (3)	1.77 (3)	2.719 (2)	170 (3)

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + 1$; (ii) $x, y + 1, z$.

For all compounds, the C-bound H atoms were placed geometrically [C—H bond lengths of 1.00 (methine CH), 0.99 (ethylene CH₂) and 0.95 Å (Ar—H)] and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The N-bound H atoms were located in a difference map and their coordinates allowed to refine freely, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$.

The whole-molecule disorder of one of the cinnamate anions in (IIIb) was modelled by finding alternative positions for all the atoms in the molecule. The corresponding bonded distance and the one-angle nonbonded distances in the two disorder components were restrained to have similar values, subject to s.u. values of 0.01 and 0.02 Å, respectively. For the carboxylate groups, the bond lengths and angles were restrained to the values of the second cinnamate anion, which was ordered. Refinement of the site occupancies gave values of 0.583 (5) and 0.417 (5). The C—C bonds involving disordered atom C12B were restrained to have similar lengths, subject to an s.u. value of 0.01 Å. The atomic displacement parameters for C12B were large, but further restraints on this atom were ineffective. For the two cycloheptane cations, the disorder of the C12 and C15 atoms in cation N1, and of C28 and C31 in cation N2 was resolved by finding alternative positions for the two atoms in a difference Fourier map; they were then refined anisotropically together with their site occupancy, such that the sum of the occupancies summed to one. Refinement of the site occupancies gave values of 0.835 (3) and 0.165 (3) for cation N1, and values of 0.616 (3) and 0.384 (3) for cation N2.

In (IIIa) and (V), the absolute structure was chosen arbitrarily, and refinement of the absolute structure parameter (Flack & Bernardinelli, 2000) led to values whose precision was too poor to enable conclusions to be drawn about the absolute structure; the Friedel pairs of reflections were thus merged prior to the final refinements.

In (IV), the diffraction data have been cut off at a 2θ angle of 47° because of weak data above this angle. The needle-like crystals were striated for this salt.

For all salts, data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM3048). Services for accessing these data are described at the back of the journal.

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